# Electrical properties and the structure changing of polycrystalline materials from the system Cu-As-Ge-S at high pressure

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**Abstract.** The results of experimental studies of magnetoresistance of polycrystalline materials $(GeS)_{1-x}(CuAsS_2)_x$ under high pressure (up to 50 GPa) are presented. The appearance of large negative magnetoresistance was found. The structure changing during applying high pressures was studied.

## 1. Introduction

Multicomponent semiconductors based on copper chalcogenids are well known as promising for fundamental and applied research materials, one of the interesting features of which is appearance of negative magnetoresistance [1,2]. Polycrystalline chalcogenides $(GeS)_{1-x}(CuAsS_2)_x$ $0.1 \leq x \leq 1.0$ are promising materials for fundamental and applied research, because of its interesting electrical properties, in particular they combine semiconducting properties with ionic and mixed (electronic-ionic) electrotransfer and other interesting features [3-7]. The temperature, time and pressure dependences of the AC and DC electrical properties of these materials have been studied in [3-7]. This work is aimed to study of pressure dependences (up to 50 GPa) of magnetoresistance and to determine a correlation between the structure changing and detected negative magnetoresistance for materials $(GeS)_{1-x}(CuAsS_2)_x$ with x =0.3; 0.4; 0.6.

## 2. Materials and experimental details

Polycrystalline materials $(GeS)_{1-x}(CuAsS_2)_x$ were synthesized by melt crystallization processes. The initial high-purity (no worse than special purity grade) components were melted in the regime of step-by-step heating in quartz ampoules evacuated to a residual pressure of $10^{-4}$ Pa, filled with superhigh-pure helium or argon [3]. These materials crystallize in cubic or tetragonal syngonies depending on the composition and show mixed (electronic-ionic) conductance with the part of ionic conductivity from 0.15 up to 0.4 [3,4]. AC electrical properties of these materials at atmospheric and high pressures are already well studied [3,4]. Current work is devoted to investigation of magnetoresistance of $(GeS)_{1-x}(CuAsS_2)_x$ with x=0.3; 0.4; 0.6, which crystallize in tetragonal syngony [3].

The baric dependences of electric properties was studied in pressure range 15-50 GPa using an equipment with high pressure cells with a rounded coneplane-type anvils made of carbonado-type artificial diamonds. These anvils with good conductivity make it possible to examine the electrical properties of samples placed into high pressure cell [8]. The equipment allows high-pressure measurements in transverse magnetic field up to 1 T and at temperatures from 78 K to room temperature. High-pressure electrical measurements were made using samples with a diameter of ~0.2 mm and thickness from 10 to 30 μm. The samples were obtained by compression in high pressure cell of the initial powdered materials. Magnetoresistance measurements at ambient pressure and room temperature were carried out for bulk samples using the cell with cooper electrodes.

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X-ray diffraction experiments at high pressures were carried out on a special diffractometer consisting of a high-flow X-ray generator FR-D, a focusing optical system Flux Max, and a BrukerAPEX CCD detector at the Institute of Geochemistry and Geophysics, University Bayreuth (Germany), in a high pressure cell with diamond anvils.

## 3. Results and discussions

It was found that electroresistance of studied materials decreases with increasing of pressure (*P)* (figure 1). Analyses of experimental results show that in magnetic field 0,75 T and more in pressure range 20-40 GPa materials exhibit negative magnetoresistance (MR), and there are one or several extremes at curves *MR*(*P*). The pressure dependences of magnetoresistance for $(GeS)_{1-x}(CuAsS_2)_x$, x=0.3 are shown in figure 2 and typical field dependences for these materials are presented in figure 3. Baric ranges of *MR*(*P*) curve extremes are correspond to baric ranges in which features of behaviour of electrical properties in AC electrical field were observed [4]. The field dependences of magnetoresistance of $(GeS)_{1-x}(CuAsS_2)_x$, x=0.3, at pressures 26 GPa and 30 GPa were studied additionally at temperature 78 K (in figure 4 results obtained under pressure of 26 GPa are shown). We can see that at low temperature effect of negative magnetoresistance is also observed.

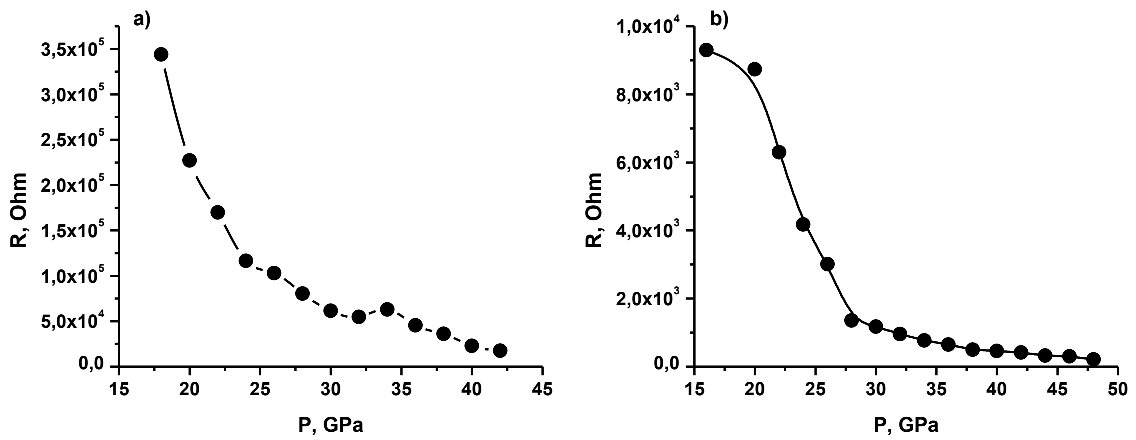


**Figure 1.** Pressure dependence of electroresistance for $(GeS)_{1-x}(CuAsS_2)_x$ a) x=0.3, b) x=0.4.

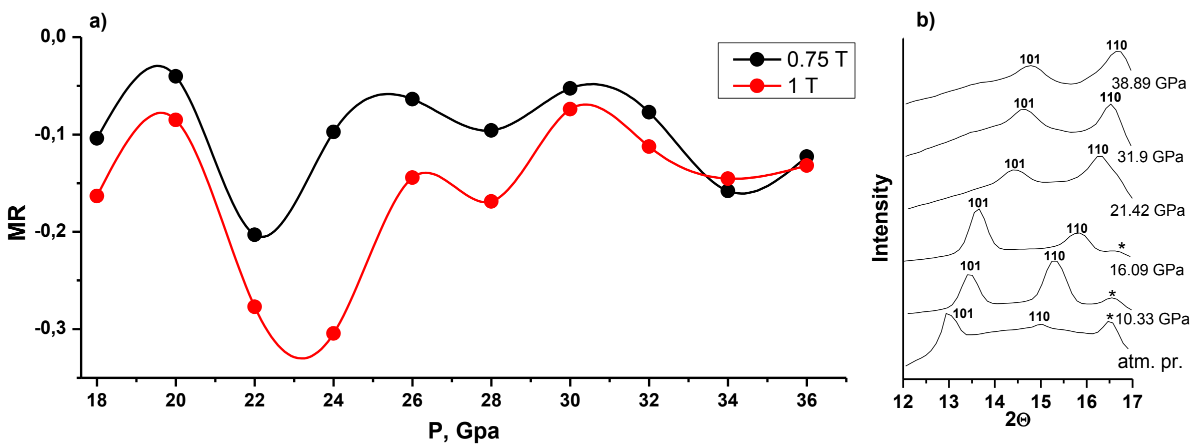


**Figure 2.** a) Baric dependence of magnetoresistance and b) results of X-ray study ( peak tagged * corresponds to Re-gasket) for $(GeS)_{1-x}(CuAsS_2)_x$, x=0.3

The origin of negative magnetoresistance (NMR) in nonmagnetic semiconductors is still subject for discussion and studies. Some authors suggest that appearance of NMR is connected with splitting of impurity levels in a magnetic field [9], some other authors connect the NMR appearance with material loose structure and small carries mobility [11]. Other theory connects NMR appearance with baric or temperature structure phase changes or significant structural defects caused by changing of external parameters [1, 12-13]. Current work authors take the view that in case of NMR in polycrystalline chalcogenide semiconductors the latter theory is more probable explication. For this theory confirmation the X-ray experiments for compound $(GeS)_{1-x}(CuAsS_2)_x$, x=0.3 were run at pressures up to 45 GPa. This material crystallizes in tetragonal syngony and at atmospheric pressure has lattice parameters a = 0.376 nm, c = 0,521 nm. It was found that pressure ranges which correspond to features of behavior *MR*(*P*) (see figure 2) are in agreement with pressure intervals with significant changing of lattice parameters.

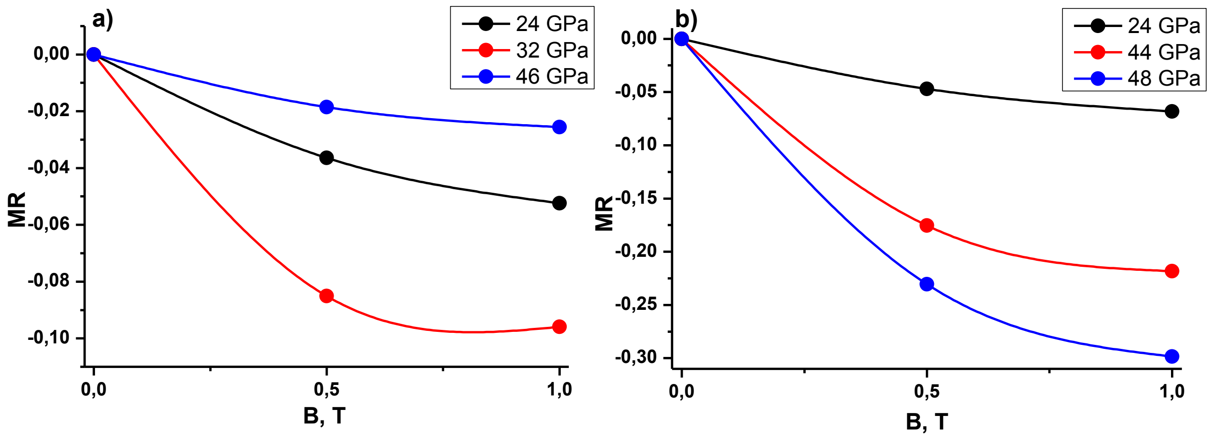


**Figure 3.** Field dependences of magnetoresistance at pressures up to 50 GPa for $(GeS)_{1-x}(CuAsS_2)_x$ a) x=0.4, b) x=0.6

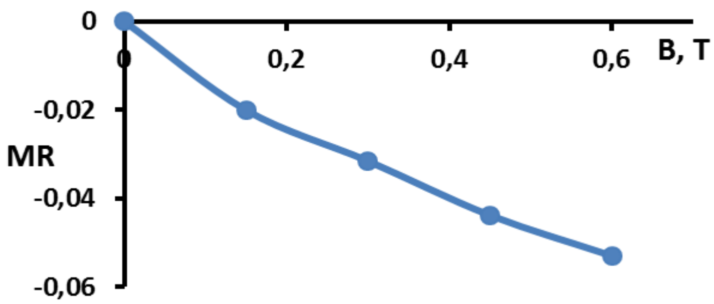


**Figure 4.** Field dependence of magnetoresistance for $(GeS)_{1-x}(CuAsS_2)_x$, x=0.3, at pressure 26 GPa at 78 K.

**Table 1.** The distances between lattice planes (101) *d* and the relative change *d* on the unit pressure at different pressures.

| P, GPa | *d*, nm (101) | Δd/ΔP |
|---|---|---|
| atm. pr. | 0.317 | |
| 10.33 | 0.307 | 0.0010 |
| 16.09 | 0.301 | 0.0010 |
| 21.42 | 0.286 | 0.0028 |
| 31.9 | 0.278 | 0.0008 |
| 38.89 | 0.276 | 0.0003 |

On the X-ray patterns (figure 2b) we can see the significant changes in position of lines, corresponding to reflections from crystallographic planes (101) and (110) at pressure range from 16 GPa to 22 GPa. In table 1 the data for the distances between lattice planes (101), which correspond to the most intensive peak on the X-ray patterns, are presented. It should be mentioned that at atmospheric pressure material shows small (near zero) MR then at pressures more than 18 GPa this material shows huge negative MR and there is maximum of MR absolute value near 22 -24 GPa (figure 2 a). Significant changes in impedance behavior for this material were observed at pressure range about 22-24 GPa [1]. All descried results can be interpreted as that at structure changing the formation of large number of defects cause changing in electronic structure of material which in turn cause appearance of visible NMR. Similar situation for polycrystalline cupper chalcogenide $CuInS_2$, $CuInSe_2$ were described in work [1], where extremes of MR(P) curve correspond to the structure phase transition.

## 4. Conclusion

Polycrystalline materials $(GeS)_{1-x}(CuAsS_2)_x$ show huge negative magnetoresistance at high pressure. The pressure and field dependences of magnetoresistance and results of X-ray diffraction study were analysed and the presence of negative magnetoresistance was suggested as consequence of changing of crystal and electronic structure.

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